

PATENT SPECIFICATION

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DRAWINGS ATTACHED.

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COMPLETE SPECIFICATION.

Process for Producing Ketones.

We, Esso RESEARCH AND ENGINEERING COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of 5 Elizabeth, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement :—

This invention relates to the production of aliphatic ketones in a single phase process utilizing electrochemical oxidation. According to one embodiment of the invention, the 15 ketone is produced by the electrochemical oxidation of the corresponding secondary alcohol. According to a second embodiment of the invention, an olefin is used as starting material and converted directly to the corresponding ketone in a single phase process 20 using electrochemical oxidation.

Ketones are produced commercially by catalytic dehydrogenation of the corresponding secondary alcohol. Ordinarily, the 25 secondary alcohol feedstock is produced by sulfuric acid hydration of the corresponding olefin. Thus, where the ketone is derived from an olefin, two separate processes with intermediate product recovery are employed. In the first such process, i.e. for alcohol 30 production, the olefin is absorbed into a concentrated sulfuric acid solution resulting in the formation of an organic sulfate which, in turn, is hydrolyzed to the corresponding secondary alcohol. The alcohol is separated 35 from the acid solution and purified by conventional separation techniques usually involving a series of distillations and caustic washings. In the second process, i.e. for ketone production, a highly refined alcohol, e.g. 99% purity or better, is passed in vapor

phase over a solid catalyst at elevated temperatures in the range of 650° F. to 45 900° F. to dehydrogenate the alcohol feedstock to the corresponding ketone. The crude ketone product is then subjected to a series of product recovery steps, the second such series in the over-all process.

The problems inherent in conventional 50 two-stage production of ketones include the necessity for separation, recovery and finishing of both an intermediate and an end product, the complexity and duplication of processing apparatus and equipment, and the need for large-scale acid reconcentration.

Electrochemical conversion of the chemical 55 energy of hydrogen or an organic compound having a lower state of oxidation than carbon dioxide to electrical energy is known in the art and a device wherein such conversion is accomplished has become commonly known as a fuel cell.

The fuel cell includes at least one fuel 60 electrode and at least one oxygen electrode, an electrolyte providing means for ionic transfer between such electrodes, means for admitting an oxidizing gas into dual contact with electrolyte and oxygen electrode, means for admitting fuel into dual contact with electrolyte and fuel electrode, and conducting means for transferring electrons from such fuel electrode to such oxygen electrode external to the electrolyte. The terms "anode" and "fuel electrode" are used interchangeably herein as are the terms "cathode" and "oxygen electrode".

The over-all fuel cell reaction is the sum 65 of two essentially independent half-cell reactions. At the anode, hydrogen, carbon monoxide, or a carbon and hydrogen comprising compound is oxidized with a release 70 of electrons to the anode. At the cathode,

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oxygen is reduced upon accepting electrons and water is formed at the cathode in an acid system with hydrogen ions from the electrolyte. The internal portion of the electrical circuit is completed by ion transfer between such electrodes while electron transfer from anode to cathode external to such electrolyte completes the electrical circuit.

It has now been discovered that the selective conversion of an olefin or a secondary alcohol to the corresponding ketone can be carried out in a fuel cell with simultaneous generation of electrical energy or in a power-consuming electrolytic cell with evolution of hydrogen. The use of an oxygen or air breathing fuel cell is preferred. The processes for production of ketones in an electrochemical cell may be carried out either continuously or as a batch process at ambient temperatures and pressures. However, it should be understood that the advantages of continuous processing within the scope of this invention are not merely the conventional advantages of increased production and efficiency of handling. The agitation of the reaction mixture in embodiments utilizing removal of electrolyte in product recovery with recycle after product separation advantageously affects the rate of reaction. In both types of reactors the organic feedstock to be converted is brought into dual contact with an aqueous sulfuric acid electrolyte and an anode of the cell. In the fuel cell the reaction is initiated by the admission of oxygen gas into dual contact with a cathode and the electrolyte which results in a catalyzed reduction of such oxygen, i.e. acceptance of electrons, and the formation of water thereafter with hydrogen ions in the electrolyte. Conducting means are provided between anode and cathode external to the electrolyte providing a net flow of electrons to the cathode after reaction is initiated. In the electrolytic cell the reaction is initiated by admitting a direct current to the cathode.

The anodic half-cell reaction, although requiring a complementary cathodic half-cell, is essentially independent of the cathodic half-cell reaction under the conditions of reaction employed in accordance with this invention. Thus the electrochemical reaction of the present process whereby ketones are produced may be referred to simply as anodic oxidation without differentiation as to the activation of the cathodic half-cell reaction. Likewise, the cell employed herein may be referred to as an electrochemical reactor, it being understood that such term herein defines a class of cells which include both a power-generating fuel cell and a power-consuming, hydrogen evolving, electrolytic cell.

The terms "electrolyte" and "sulfuric acid electrolyte" as employed herein refer to the combination of H_2O and H_2SO_4 , and

concentrations thereof are based upon this two-component system. The term "electrolyte solution" as employed herein refers to the electrolyte of H_2O and H_2SO_4 , together with dissolved organic compounds therein, i.e. alcohol and/or olefins. 70

The concentration of the sulfuric acid electrolyte employed in the process of this invention in its broadest aspects is in the range of 0.5—12 moles of H_2SO_4 /liter of electrolyte ($H_2SO_4 + H_2O$); preferably 6—11.5 moles H_2SO_4 /liter, and more preferably a concentration of 9—10.5 moles H_2SO_4 /liter. 75

High selectivity to ketone production is promoted by controlling the oxidation potential or voltage at which the feed is converted. Thus, the oxidation potential maintained is insufficient to effect evolution of oxygen, e.g. at an anodic variation relative to standard hydrogen reference in the range of 0.5 to 1.65 or slightly greater in dilute acid. 80

In the practice of this invention as a continuous process, production rates are maximized while maintaining a high selectivity to the ketone product by rapid removal of the ketone product from the sites of reaction so as to avoid a buildup of ketone in the electrolyte contacting the one or more anodes of the cell. This is of critical importance where the ketone is acetone. In the production of acetone in accordance with this invention a low ketone to alcohol ratio is maintained in the electrolyte, e.g. in the range of from 1/20 to 1/100 or smaller, 90 preferably not greater than 1/50. With higher molecular weight ketones it surprisingly has been found that much higher ketone to feed ratios will not adversely affect the reaction, e.g. 3/1 or greater. 100

In batch processes selectivity to the ketone product may be obtained by calculating the degree of conversion from the total quantity of electricity flowing from the anode of the cell and limiting the reaction time. 105

Control of ketone concentration in the electrolyte may be maintained by continuously removing electrolyte from the cell, separating the ketone product from the electrolyte and unreacted feed by conventional separation techniques such as distillation, extraction, etc., with the electrolyte and unreacted feed recycled to the cell. In an alternative method, the product may be separated from the electrolyte by operating 115 the cell with an electrolyte temperature that admits of distillation directly from the cell. 120

In the present process, the conditions of reaction may be controlled to favor electrochemical reaction over chemical reaction 125 and through this and control of product removal the high selectivity to the desired ketone is achieved. High selectivity to the ketone product requires preservation of the original carbon skeleton of the feed both 130

during and after formation of the ketone product. The operating temperature is preferably controlled to provide a high rate of conversion of the alcohol or olefin feed 5 while avoiding oxidation of any significant quantities of the ketone product. Thus, expressed in functional terms the reaction should be carried out at a fuel cell temperature above the initiation temperature required for self-starting of a fuel cell reaction 10 and below the corresponding temperature at which anodic oxidation of the corresponding ketone is initiated. In certain embodiments, however, where a greater output of electrical energy product is desired a portion of the ketone product may be oxidized to carbon dioxide which will eject itself from an acidic electrolyte. In general, the process is preferably carried out at a temperature between 15 75° F. and 250° F., and most preferably between 120° F. and 185° F. Conversion is obtainable as low as 35° F. with some sacrifice in the rate of reaction.

In the practice of this invention, conventional fuel cell apparatus may be employed. The vessel should be constructed of a material 25 resistant to the electrolyte employed at the temperature of operation. Suitable materials include stainless steel, glass, earthenware, and various polymeric solids. Where the vessel is constructed of stainless steel or other conductive material, insulation in accordance with conventional electrical circuitry would be employed to avoid short-circuiting between 30 the electrodes.

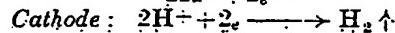
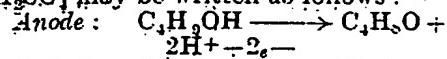
The electrolyte provides ionic conductance 35 between anode and cathode and may be divided by an ion permeable fuel barrier, e.g. an ion exchange membrane, into an 40 anolyte and catholyte. In a cell so divided the feed is admitted to the anolyte. In an undivided electrolyte the fuel is in free circulation in the single electrolyte. Conducting means are employed to establish electrical 45 connection between anode and cathode external to the electrolyte. The oxidizing gas, e.g. pure oxygen, air, other mixtures of oxygen with inert gases such as nitrogen, etc., is admitted to the interface formed at the 50 meeting of cathode with electrolyte. With this admission of oxygen to the cathode and contact of feed-electrolyte solution with the anode at the temperatures of operation hereinbefore set forth an electrochemical reaction is 55 initiated. Electrons are released upon the surface of the anode upon dehydrogenation of the feed and there is a net flow of such electrons to the anode through a resistance. Electrical power so generated in passing 60 through such resistance may be recovered as useful work. The ketone product formed by such dehydrogenation may be recovered from the electrolyte by one of the means hereinbefore discussed.

65 Conventional fuel cell electrodes may be

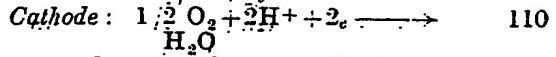
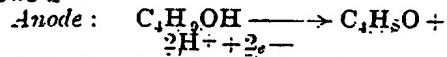
employed comprising, for instance, a porous carbon base impregnated with the desired metal-containing catalyst, a porous metal sheet, or a metal base of the desired configuration upon which a suitable catalyst has been deposited.

In an acid medium both the anode and cathode catalysts are preferably platinum comprising catalysts and may be deposited upon carbon or employed over a metal base. The term "platinum comprising catalysts" as used herein includes platinum alone and in admixture with other noble metals, especially gold and/or iridium. Other conventional fuel cell catalysts, however, may be used choosing materials not attacked by the electrolyte employed.

In the practice of this invention in an electrolytic cell, i.e. wherein electrical energy requisite for the dehydrogenation reaction is supplied from an outside source, essentially the same equipment may be employed. In this embodiment a source of direct current is connected to the cathode of the cell and the admission of oxygen to the cathode to activate the cathodic half-cell reaction eliminated. The operational potential as well as the other operating conditions are maintained within the ranges hereinbefore set forth in discussing the reaction in a true fuel cell system. In this process hydrogen is evolved from the electrolyte and may be recovered overhead by conventional means. The reactions of this embodiment in the conversion of secondary butanol to methyl ethyl ketone 100 in H_2SO_4 may be written as follows:



In contrast the same alcohol conversion in a fuel cell system may be expressed as follows:



In accordance with one embodiment of the invention, the alcohol feedstock is placed in solution in the aqueous electrolyte. Ordinarily, this electrolyte will consist 115 essentially of water and sulfuric acid. Any substance may be included in the solution, however, which does not adversely affect the electrochemical dehydrogenation of the alcohol feed to the ketone product or adversely 120 affect the over-all operation of the electrochemical reactor.

The secondary alcohol feedstocks of the present invention preferably consist of those secondary alcohols having an appreciable 125 solubility in the aqueous electrolyte at operating temperatures and pressures without the addition of mutual solvents, e.g. lower molecular weight alcohols, or emulsifiers. The solubility of secondary alcohols 130

in aqueous solutions of sulfuric acid increases with the concentration of H_2SO_4 therein and C_3-C_9 aliphatic secondary alcohols are particularly suitable feedstocks for this process.

5 Alcohols up to C_{12} or higher can be converted to ketones in accordance with this process by employing various operational techniques including operation at elevated pressures, the use of mutual solvents, e.g. ketones of

10 the same or lower molecular weight or lower molecular weight alcohols, emulsification, agitation of electrolyte, etc.

The concentration of alcohol in electrolyte in the process of this invention may vary over a wide range from minimum amounts necessary to sustain cell activity and maintain ketone production up to solubility limits of the chosen alcohol feed in the electrolyte employed. The choice of concentration will 15 be somewhat affected by solubility of the alcohol feed and the temperature of operation. However, an adaptability to provide reasonably high rates of electrochemical dehydrogenation coupled with considerations for selectivity of conversion to ketone product constitutes the controlling criteria. The alcohol concentration in electrolyte should preferably be in the range of from 0.5 to 5 moles per liter or greater, particularly desirable are concentrations in the range of from 5-8 20 moles/liter.

According to another embodiment of the present invention, the selective electrochemical production of aliphatic ketones can 25 be obtained from the corresponding olefin without the separation of any intermediate product. According to this embodiment, an olefin is contacted with an aqueous sulfuric acid solution, the acid solution employed as 30 the electrolyte of an electrochemical reactor, and the absorbed olefin and/or a hydration derivative thereof converted to the corresponding ketone. The process may be carried in a fuel cell system from an olefin comprising feedstock in a sulfuric acid medium with the simultaneous production 35 of a ketone and electrical energy or in an electrolytical cell with the production of a ketone and pressurized hydrogen of high 40 purity. The ketones may also be produced from normal olefins contained in a hydrocarbon mixture which also contains iso-olefins by selectively extracting such iso-olefins from such mixture and sending such 45 n -olefins directly to the sulfuric acid electrolyte of an electrochemical reactor as a gas or liquid.

Referring to the accompanying drawings, Figure 1 is a schematic side view of a simplified fuel cell which may be utilized as an electrochemical reactor for carrying out one embodiment of this invention.

Figure 2 is a schematic side view of a simplified electrolytic cell which may be utilized as an electrochemical reactor for

carrying out another embodiment of the present invention.

Figure 3 is a schematic flowplan illustrating processing of a mixed hydrocarbon stream in the production of ketones in 70 accordance with this invention.

While Figures 1 and 2 are equally applicable with either an olefin or an alcohol feed, the following specific discussion will be limited to the use of an olefin feed.

In Figure 1 there is shown a vessel 1 containing an aqueous sulfuric acid electrolyte. Cathode 2 divides vessel 1 into an electrolyte zone 3 and an oxygen receiving compartment 4. Compartment 3 is here shown divided into an anolyte compartment 3A and a catholyte compartment 3B by an electrolyte divider 5. This divider may be an ion-exchange membrane, a porous glass plate or other means admitting of ion transfer but suitable for retaining in the anolyte, a major portion of the organic materials admitted to compartment 3A, e.g. olefins and their reaction products. Divider 5 is not essential to the process but improves reaction rate if the cathode employed is adversely affected by contact with the organic reactant. Cathode 2 is a porous carbon plate impregnated with a platinum comprising catalyst, e.g. 95% platinum and 5% gold. The larger pores of this electrode are coated with a suitable wetproofing agent, such as polytetrafluoroethylene. Within anolyte compartment 3A is positioned anode 6, an acid resistant metal sheet surfaced with a coating of platinum black. It is preferred to employ at each electrode a platinum-comprising catalyst which may be platinum alone or an alloy, or mixture of platinum with other metals, particularly gold and/or iridium. In 85 such mixtures platinum is the major component by weight while the other metal or combination of other metals constitutes a minor component by weight, e.g. 1 to 10%. However, it is within the scope of this invention to employ any of the acid resistant fuel cell catalysts known to the art for use in the reduction of oxygen at the cathode or oxidation of an organic compound at the anode.

In one embodiment of the invention air is 90 passed into oxygen receiving compartment 4 via conduit 7 in an amount preferably in the range of from 50 to 200% of the stoichiometric requirements of the fuel cell reaction. Oxygen diffuses through porous cathode 2 and forms with the electrolyte and cathode 2 a three-phase contact or interface. Excess air, oxygen, depleted air and absorbed water vapor is exhausted from compartment 4 via conduit 8. A n -olefin, e.g. butene-1, is 95 admitted to the anolyte via conduit 9 as a gas and absorbed by the sulfuric acid therein. The resulting solution containing the hydration products of such union of acid and olefin is brought into contact with anode 6 where 100

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- ketone, in this case methyl ethyl ketone, is formed. When oxygen is in contact with the electrolyte at the reaction sites on cathode 2, the olefin-acid comprising solution 5 is in contact with the reaction sites on anode 6. Wires 10 and 11 are conductors from electrodes 6 and 2, respectively, and together with a resistance means 12 complete the electrical circuit. Resistance means 12 may 10 be any power-consuming device for utilizing the electrical output of this process and, if desired, may be nothing more than the conductor establishing electrical connection between the electrodes.
- In this embodiment the cell may be operated so as to remove the ketone overhead via conduit 13 at a temperature sufficient to give a significant vapor pressure of the ketone above the electrolyte. The product 15 in conduit 13 together with other vapors carried overhead from the cell is passed to a product recovery zone for separation and purification external to reactor vessel 1. However, it is to be understood that the process may be carried out so as to remove the ketone as a liquid by continuously withdrawing electrolyte, separating product and recycling the electrolyte to the reactor. It is also within the scope of this invention to absorb the olefin in the electrolyte outside the cell, introducing both in a common stream. It is within the scope of this invention to channel the product recovery stream from a large number of cells to a common 20 recovery unit.
- It is further to be understood that although the reactor of Figure 1 is an operable device for practicing this invention, it is a greatly simplified adaptation of apparatus that would be used for large-scale production and that a 25 large number of such cells may be connected either in bipolar or unipolar arrangement in series and/or parallel to provide an industrial reaction unit.
- In Figure 2 a power-driven electrolytic cell is utilized for a different embodiment wherein an olefin absorbed stream of aqueous sulfuric acid is admitted to reaction vessel 21 via conduit 20. In the alternative, the 30 olefin may be admitted to electrolyte in 21 as a gas via conduit 20. The electrolyte concentrations applicable for use in the fuel cell aforescribed are equally applicable to this reactor. Positioned within vessel 21 are anode 22 and cathode 23 comprising metal sheets upon which has been electrodeposited a coating of platinum black. Electrodes 22 and 23 are connected with wires 24 and 25, respectively. Wires 24 and 25 pass out of vessel 21 through insulators 26 and 27, respectively, and are connected with a direct current electrical power source 28. Power source 28 may be any source of direct electric current, e.g. storage battery, power-producing fuel cell pack, rectified alternating current, etc. Electrical energy, e.g. with a potential of from 0.5 to 1.65 volts, is admitted to cathode 23 from power source 28 and the conversion of the absorbed olefin to ketone, as hereinbefore described, is initiated at anode 22. When electrical energy is admitted to cathode 23, as before mentioned, hydrogen gas is evolved from the electrolyte solution (aqueous H₂SO₄) at cathode 23 and such gas exits from the cell via conduit 29. A pressure control valve may be associated with conduit 29 providing means for utilizing the hydrogen evolved to pressurize the reactor and to permit recovery of high pressure hydrogen. Baffle 30 is positioned across the top of the reactor so as to extend below the upper surface of the liquid electrolyte-reaction mixture or solution. Baffle 30 is so positioned to prevent any appreciable transfer of hydrogen evolved at cathode 23 to anode 22 where it would react electrochemically. A side stream comprising ketone, secondary alcohol, the corresponding organic sulfate, olefin and sulfuric acid is removed continuously from reaction vessel 21 via conduit 31 and passed to a product recovery unit. As in the fuel cell, reactor product may be recovered overhead as a gas when the product and the conditions employed make that possible. Product recovery may be effected by distillation, extraction and other conventional liquid separation techniques. The acid, olefin, sulfate and secondary alcohol may be recycled to the cell after separation of the ketone.
- If the starting material used is a secondary alcohol instead of an olefin then the conduits shown in Figures 1 and 2 for the introduction of the olefin will be used to introduce the alcohol.
- Referring to Figure 3, a refinery stream comprising a mixture of hydrocarbons containing iso-olefins and n-olefins is passed via conduit 41 to iso-olefin extractor 42. This stream ordinarily will consist mainly of hydrocarbons having the same number of carbon atoms per molecule, e.g. a mixed C₄ stream containing isobutylene, n-butylene, n-butane and isobutane. Hydrocarbon streams containing both n-olefins and aromatics preferably should be pretreated, e.g. with a selective solvent such as phenol, to remove the aromatics before carrying out the present process. When minor amounts of hydrocarbons of different carbon number are present in the feedstock, their concentration should be minimized so far as the economics of separation permit. The iso-olefin extractor 42 comprises one or more, normally three, reactors or mixers each followed by an emulsion settler, an emulsion circulation pump and coolers. Alternatively the iso-olefin may be extracted from the mixed hydrocarbon stream in a countercurrent operation employing a packed tower. In

- 5 this unit the hydrocarbon mixture is contacted in liquid phase with 60 to 70, preferably 63 to 68 and most commonly 65, wt. % sulfuric acid to extract the iso-olefin. This extraction is preferably carried out at from 70° F. to 110° F. to yield an iso-olefin acid extract. In the case of a C₄ stream an extract is removed containing from 1.3 to 1.4 moles of isobutylene/mole of H₂SO₄, and the extraction is carried out in stages at temperatures in the range of 70° F. to 100° F. Contact of the hydrocarbon mixture with such acid includes countercurrent flow and or jet mixing. The reaction of an iso-olefin with sulfuric acid is much faster than that of the corresponding n-olefin under these conditions. Holdup time in iso-olefin extractor 42 can therefore be terminated before any appreciable quantity of n-olefins is absorbed. The iso-olefin/acid extract is removed from iso-olefin extractor 42 via conduit 43 and passed to iso-olefin regeneration and recovery unit 44, while the unabsorbed remainder of the mixed hydrocarbon stream, i.e. n-olefins and paraffins, is passed as via conduit 45 to electrochemical reactor 50. This stream may be vaporized in a separate subunit of extractor 42 or at any point between extractor 42 and reactor 50.
- 10 Regeneration unit 44 ordinarily will comprise a degassing drum and a regenerator tower which are not individually shown in the drawing. The iso-olefin/acid extract is normally heated by the injection of steam and passed to the degassing drum to flash off paraffins which take with them some olefins. The degassed extract is then pumped to the regenerator tower where water is injected into the top of such tower to control the top temperature while a steam spray is admitted at the bottom thereof to maintain a temperature of 250° F. An overhead stream from regeneration unit 44 is passed via conduit 46 to an iso-olefin finishing unit, not shown. The sulfuric acid in regeneration unit 44 may be diluted in the recovery of iso-olefins to 45 wt. % or less and this diluted acid is passed via conduit 47 to acid reconcentration unit 48 where it is reconcentrated by means well known in the art, e.g. distillation, to the desired 60 to 70 wt. %, preferably 65 wt. %. Reconcentrated acid may be recycled via conduit 49 to iso-olefin extractor 42 or passed via conduit 63, valve 59, and conduit 60 to electrochemical reactor 50 for use as electrolyte therein. Electrochemical reactor 50 comprises at least one, and preferably a plurality of fuel cells or electrolytic cells which may be connected in series and/or parallel. Each individual cell in such reactor comprises an anode and a cathode which are spaced apart with a sulfuric acid electrolyte providing means for ion transfer between such electrodes. The cell packs may be
- 15 constructed so as to connect cells to each other by either simple unipolar connection between anode and cathode or bipolar connection for series connection wherein conduction is provided from one electrode of one cell to the opposite electrode of another with single terminal conductors at opposite ends of the cell pack forming the terminal leads for an external circuit. The cathode of the fuel cell will preferably comprise a porous acid resistant structure through which oxygen can diffuse to contact the electrolyte, e.g. porous carbon impregnated with an acid resistant metal catalyst, a porous organic membrane that is acid resistant and which has been surfaced with a continuous layer of acid resistant metal to serve as both the electrode conductor and catalyst, or porous metal structures suitably designed. The cathode of the electrolytic cell need only be of an acid resistant material which is a good electron conductor and may take the form of a metal sheet or grid. It may be coated with a suitable catalytic salt or metal to reduce the voltage required for the cathodic process in a manner well known in the art. The anode requirements are the same for both the fuel cell and the electrolytic cell. Since the reactant feed is soluble in the electrolyte there is no necessity to employ a porous or diffusion type anode to bring the ketone yielding material into simultaneous contact with the anode and the electrolyte. However it is often advantageous to employ porous structures to obtain a greater number 20 of reaction sites per unit area.
- 20 The cell or cells may be operated at temperatures as low as room temperature and below, e.g. 35° F., at atmospheric pressure to temperatures in the range of 300° F. to 400° F. It is preferred, however, to operate at temperatures in the range of from 75° F. to 250° F. and, more preferably, in the range of 120° F. to 185° F. Operation at atmospheric pressure eliminates the complexities inherent in designing and controlling a pressure resistant reactor but certain reaction rate advantages are to be obtained at elevated pressure, e.g. between 1 and 50 atmospheres. While temperatures below 75° F. provide a clean, highly selective reaction, the rate of reaction is markedly decreased. Care must be exercised when operating at the higher temperatures mentioned, i.e. above 180° F., to control acid concentration and product removal to avoid excessive polymer formation, etc.
- 25 Makeup water or water for dilution may be admitted to reactor 50 via conduit 61, valve 62 and conduit 60.
- 30 Ketone product, together with the much less reactive paraffins in the stream, may be removed from electrochemical reactor 50 with electrolyte via conduit 51 and passed to a product recovery unit 54 where the 35
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5 paraffins and ketone are separated from the electrolyte which is recycled to the reactor via conduit 58, valve 59 and conduit 60 to electrochemical reactor 50. The paraffins are separated from the ketone product and passed from the system via conduit 56. A crude ketone product which includes secondary butanol is passed via conduit 55 to a ketone finishing or purification unit, not shown. The secondary alcohol may be recycled either from unit 54 or the aforementioned finishing unit to the electrochemical reactor. In the alternative, electrochemical reactor 50 may be operated so as 10 to remove the ketone product overhead as a gas or vapor stream via conduit 57 and thence to product recovery unit 54. In this embodiment the relatively unreactive paraffins pass overhead with the ketone and facilitate recovery of the ketone functioning as a stripping gas.

When the process of this invention is carried out in an electrolytic cell that consumes electrical energy supplied from an outside source, the electrical energy supplied to the cathode is controlled so as to be insufficient to initiate oxygen evolution from the electrolyte so as to avoid undesirable side reactions. This will allow for a cathode potential of 1.65 volts anodic with respect to standard hydrogen reference or slightly higher depending upon the acid concentration of the electrolyte and the process will ordinarily be carried out in the range of from 25 0.5 to 1.6 volts anodic to such reference. The process in the electrolytic cell is conducted so as not to effect any material change from the anodic half-cell reaction occurring when the process is carried out in a power-producing fuel cell.

In the choice of an olefin feedstock for use in the process of this invention, the highest selectivity to a single ketone product is obtained by employing the corresponding normal olefin. Thus propylene is employed for the production of acetone, butene-1 or butene-2 for producing methyl ethyl ketone, the n-pentenes for producing methyl propyl ketone and diethyl ketone, the n-hexenes for producing methyl butyl ketone and ethyl propyl ketone, etc. It is within the scope of this invention to preabsorb the olefin into the aqueous sulfuric acid solution external to the reactor so that the olefin feed and the acid electrolyte are admitted to the electrochemical reactor combined in a single solution. It is also within the scope of this invention to introduce the electrolyte and the olefin separately to the reactor as by 40 passing olefin gas into the electrolyte either within a zone in communication with the anode of the cell or within a separate compartment within the cell from whence the resulting solution may be circulated after contacting the anode. When the olefin feed

is fed continuously to the cell as a separate stream, absorption will, of course, occur at the operating temperature of the cell, i.e. the electrolyte temperature. The temperature employed should take into consideration the acid concentration employed with the higher temperatures employed with the more dilute acid and vice versa. Excessive contact between olefin and acid should be avoided particularly at elevated temperatures and the time of contact prior to admission to the cell preferably is as short as effective extraction permits. When operated as a continuous process the ketone product may be removed from the cell as formed, and in the particular case of acetone production, should be removed as quickly as possible so as to avoid the buildup of acetone in the cell. With higher molecular weight ketones a much greater concentration of product can be tolerated within the cell without reducing the rate of electro-chemical conversion, thus making possible more flexibility with regard to products recovery. For instance, in the production of methyl ethyl ketone from n-butlenes in accordance with this process ketone to olefin and/or alcohol ratios of 3/1 and higher do not adversely affect the reaction to any noticeable degree.

With normal modifications in accordance with molecular weight, solubility characteristics, etc. the process of this invention may be effectively carried out to produce a wide variety of ketones, e.g. C₃ to C₁₂ or higher. The process is applicable to C₄ to C₉ aliphatic ketones and especially to C₄—C₆ aliphatic ketones. Various operational techniques may be employed to maintain the effectiveness of the process where the alcohol formed by hydrolysis of the absorbed olefin has a tendency to separate from the electrolyte. These include operation at elevated temperatures and pressures, control of acid concentration so that the alcohol solubility is increased with increased acid concentrations or so that the rate of hydrolysis is essentially equal to the electrochemical oxidation rate, thorough mixing of reactants and electrolyte via recycling, etc. and cell design.

In the production of certain higher molecular weight ketones by this process the ketone product will separate from the electrolyte forming a separate liquid phase. In such embodiments it is within the scope of this invention to remove such ketone from 110 this separate liquid phase as a liquid side stream from the cell essentially free of electrolyte.

EXAMPLE 1.

In a fuel cell containing an aqueous sulfuric acid electrolyte separated into an anolyte and catholyte by an "Alundum" thimble, electrical energy was generated using isopropanol fuel. ("Alundum" is a Registered

Trade Mark.) The anode employed was a platinum sheet upon which platinum-black had been electrodeposited. The cathode employed was a porous carbon cylinder impregnated with a platinum and gold catalyst containing 95% platinum and 5% gold. The initial concentration of isopropanol in

the anolyte was 1 mole per liter. The concentration of sulfuric acid in both the anolyte and catholyte was 1 mol per liter. The electrolyte was removed from the cell and analyzed. The conditions of cell operation and the results of such operation are set forth in Table I.

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TABLE I.
PRODUCTION OF ACETONE FROM ISOPROPANOL.

	Temperature, °F.	71-74
	Pressures, atmospheric, absolute	1
	Initial concentration of fuel in anolyte in mols/liter	1
20	Total weight of anolyte, in grams	145
	Concentration of H ₂ SO ₄ in electrolyte in mols/liter	1
	Reaction time, hrs.	26
	Anode surface, ft. ²	0.035
	Average current drawn (amps./ft. ² anode)	2.5
25	<i>Load Voltage.</i>					
	Anode vs. H ₂ reference electrode	0.68-0.86
	Cathode vs. reference O ₂ electrode	0.82-0.87
	Anode vs. theoretical O ₂ electrode	0.56-0.38
	Anode polarization	0.66-0.84
30	<i>Anolyte Product, Wt. %.</i>					
	Isopropanol	1.44
	Acetone	1.14
	Other organics	None by mass spectrometry
35	CO ₂ collected, grams	0.0052
	<i>Anolyte Carbon, % Found as.</i>					
	Isopropanol	54.7
	Acetone	44.8
40	<i>Products, Mol % Distribution.</i>					
	Acetone	99.7
	CO ₂	0.3

EXAMPLE 2.

To determine the effect of acetone concentration in the electrolyte on the electrochemical dehydrogenation of isopropyl alcohol varying amounts of acetone were added

to the electrolyte as the fuel cell reaction of isopropanol described in Example 1 was initiated. The effect of acetone concentration measured at a constant anode polarization are set forth in the following table :—

50

TABLE II.

EFFECT OF ACETONE CONCENTRATION ON REACTION RATE OF ISOPROPANOL IN FUEL CELL AT 0.6 VOLTS POLARIZATION.

	Mol ratio alcohol to acetone	Ampere/ft. ² anode surface
	No acetone	20.5
	100/1	14.3
	10/1	4.8
60	1/1	0.172

EXAMPLE 3.

The procedure of Example 1 was repeated except that the cell was fueled with acetone to determine the temperatures required for the further oxidation of acetone product. At room temperature (75° F.) no reaction occurred. The temperature was increased

and electrochemical reaction of the acetone was initiated at 180° F. This clearly establishes that the preferred operating range for the electrochemical production of acetone from isopropyl alcohol so as to avoid fuel loss to carbon dioxide is in the range of from room temperature to 180° F.

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EXAMPLE 4.

Other alcohols were reacted in accordance with the process of this invention. The

conditions of reaction employed and the results obtained therefrom are set forth in the following table. 5

TABLE III.

ELECTROCHEMICAL CONVERSIONS OF SECONDARY ALCOHOLS TO THE CORRESPONDING KETONES IN H_2SO_4 .

10	Alcohol	C_3 (1)	C_4 (2)	C_4 (3)	C_4 (4)
<i>Aqueous Anolyte.</i>					
	Fuel, moles/liter	..	1.0	1.0	1.0
	H_2SO_4 , moles/liter	..	1.0	0.5	0.5
<i>Catholyte.</i>					
15	H_2SO_4 moles/liter	..	3.7	0.5	0.5
	Catalyst, anode	..		Platinum black on platinum sheet	10
	Cathode	..	(3)	(3)	(4)
	Temp., °F.	..	71—74	75	180
	Reaction time, hours	..	27	45	22.2
20	Current, avg. amps	..	0.087	0.0066	0.223
	Coulombs	..	8,450	1,070	17,917
	Anode surface, ft. ²	..	0.035	0.035	0.50
	Amps. ft. ² , avg.	..	2.5	0.19	0.44
	Load Voltage vs. H_2 reference				0.15
25	Fuel anode	..	-0.77	-0.70	-0.67
	Cathode	..	-0.84	-0.73	+0.09
	Load volts polarization (5)	..	0.72	0.64	0.61
	Selectivity of reacted alcohol, mole %, to				1.05
30	CO_2	..	0.1	3.4	1.8
	Ketone	..	99.9 (6)	96.6 (7)	98.2 (7)
					90.5 (7)

(1) Isopropanol.

(2) Butanol-2.

(3) Air or oxygen breathing cathode consisting of a 2" diameter × 4" height porous carbon cylinder impregnated with a platinum-gold catalyst.

(4) A 2" diameter 52 mesh platinum screen electrode—these runs powered by rectified alternating current.

(5) Polarization below theoretical voltage for complete oxidation in the H_2SO_4 strength indicated in the anolyte.

(6) Acetone.

(7) Methyl ethyl ketone.

EXAMPLE 5.

The effect of varying current density on selectivity to methyl ethyl ketone and carbon dioxide in the process of this invention was studied by carrying out electrochemical oxidation (dehydrogenation) of secondary butanol in accordance with the general procedure of the preceding examples which employed an electrolyte cell. The course of electrical power was again rectified alternating current supplied to the cathode of the cell at a potential of 1 volt. The electrolyte employed was aqueous sulfuric acid (65 wt. % H_2SO_4) to which secondary butanol was added until the resulting solution contained 7 moles of secondary butanol per liter of

electrolyte-alcohol solution. Secondary butanol is completely miscible with aqueous sulfuric acid solutions containing above 10 wt. % H_2SO_4 at room temperature, i.e. 75° F. Complete miscibility of higher molecular weight alcohols with aqueous sulfuric acid require correspondingly higher H_2SO_4 concentrations. The anode at which such oxidation took place was a platinum sheet upon which platinum black had been electro-deposited. The current through the cell was varied by varying the resistance in the external circuit. The temperature of the electrolyte was 170° F. The effect of varying current density on product selectivity is given in the following table:—

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TABLE IV.

EFFECT OF CURRENT DENSITY ON PRODUCT SELECTIVITY IN ELECTROCHEMICAL CONVERSION OF SECONDARY BUTANOL TO MEK*.

	5	Current amps./ft. ² (1)	Mole % converted alcohol to MEK	% current attributable to CO ₂ Production
10	34.5	99.6	0.4	4.5
	34.5 (2)	99.5	0.5	5.5
	138	97.3	2.7	25.3
	230	97.9	2.1	20.6

(1) Based on superficial anode surface in contact with electrolyte solution.

(2) Confirmation run.

* MEK = methyl ethyl ketone.

15

EXAMPLE 6.

The procedure of Example 5 was repeated to determine the effect of alcohol concentration in the electrolyte solution upon current density. Runs were made with solutions of secondary butanol in aqueous sulfuric acid wherein the alcohol concentrations were respectively 6, 7, and 8 moles secondary

butanol per liter of solution. The acid concentrations are listed with each run. The electrolyte temperatures were in the range of 170°—180° F. and the pressure was atmospheric. The effect of alcohol concentration upon electrochemical reaction rates as evidenced by current density is shown in the following table:—

25.

30.

TABLE V.

EFFECT OF ALCOHOL CONCENTRATION ON CURRENT DENSITY IN ELECTROLYTE SOLUTION IN ELECTROCHEMICAL CONVERSION OF SECONDARY BUTANOL TO METHYL ETHYL KETONE.

	35	Alcohol Concentration.	Sec-butanol moles/liter	6	7	8
		Acid Concentration.				
		Wt. % H ₂ SO ₄ (Based on H ₂ O & H ₂ SO ₄ only)		55	65	65
		Open circuit voltage (1)	.. .30	.. .40	.. .36	
	40	Current Density.				
		Amps./ft. ² (2) at polarization (1) of,				
		0.8 volts	10	98	63
		0.9 volts	195	144	213
		1.0 volts	425	333	276

45 (1) vs. Standard Hydrogen Reference.

(2) Based on superficial anode surface in contact with electrolyte solution.

EXAMPLE 7.

Ketones were produced electrochemically from a variety of olefin feedstocks in the following manner: Aqueous sulfuric acid electrolytes ranging in concentration from 0.5 to 12 moles H₂SO₄/liter were employed in a power driven electrolytic cell. The anode employed in such cell was a platinum sheet upon which platinum black had been electrodeposited while the cathode was a platinum wire screen. The source of power was rectified alternating current at an average potential of 1 volt. In one embodiment electrolyte was placed in the cell and the

olefin was admitted thereto as a gas. In another embodiment the olefin was pre-absorbed in the electrolyte and admitted to the cell with the electrolyte. The gaseous effluent from the cell was continuously collected and after several hours operation this and the electrolyte were analyzed.

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The following table sets forth the conditions and resulting product distribution obtained from the conversion of three representative olefins to the corresponding ketones. In these runs the olefin was admitted to the cell as a gas.

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TABLE VI.
ELECTROCHEMICAL PRODUCTION OF KETONES FROM OLEFINS
IN SINGLE STAGE PROCESS.

	Reaction temp., °F.	Conc. of electrolyte, moles H ₂ SO ₄ /liter	Olefin feedstock	Ketone product	8 propylene acetone	10 butene-2 methyl ethyl ketone	10 pentene-2 methyl propyl ketone
5							180
							10
10	Product selectivity						
	To ketone, mole %			> 50	> 70	> 85
	To CO ₂ , mole %			22—30	8—18	8—10

15 This method of olefin feeding was compared with preadsorption of olefin in electrolyte employing butene-2 as the olefin feedstock. With acid strengths of 6—7 molar and lower preadsorption of olefin selectivity to CO₂ decreased markedly. With higher acid concentrations, e.g. 8—12 molar, the selectivity to MEK (methyl ethyl ketone) was high by both methods as shown in the following table.

TABLE VII.
ELECTROCHEMICAL PRODUCTION OF METHYL ETHYL KETONE FROM BUTENE-2
WITH PREADSORPTION AND GAS FEED INTO ELECTROLYTE OF OPERATING CELL.

	Reaction temp., °F.	Conc. of electrolyte, moles H ₂ SO ₄ /liter	Effect of method of feeding of olefin on product dist.	180	10
20					
				6	10
25	Preadsorption at 75° F.				
	Selectivity to MEK, mole %		> 60	> 75
	Selectivity to CO ₂ , mole %		6—15	9—20
	Gas feed to electrolyte.				
	Selectivity to MEK, mole %		> 70	> 75
	Selectivity to CO ₂ , mole %		23—25	8—20

30 A separate oxidation was made with butene-2 and 10 molar H₂SO₄ to determine the effect of temperature on product selectivity. The reaction temperature employed was 120° F. The selectivity to MEK was slightly increased with a corresponding decrease in selectivity to CO₂.
45

35 The foregoing procedures were repeated in a fuel cell with simultaneous production of electrical energy by substituting a porous carbon cathode impregnated with 1 wt. % platinum and gold in a 95/5 wt. ratio and gaseous oxygen was passed through such

electrode so as to form a three phase interface between electrode, electrolyte and oxygen. Product selectivity was not significantly changed as compared to the power driven cell.

EXAMPLE 8.

To further demonstrate this invention, additional runs were made in accordance with Example 7 except as herein stated; the conditions of such runs and the results obtained are set forth in the following table. The anode catalyst was platinum black for all runs.

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TABLE VIII.
ELECTROCHEMICAL PRODUCTION OF KETONES WITH DIFFERENT FEEDSTOCKS AND
REACTION CONDITIONS IN ELECTROLYTIC REACTOR.

Olefin feedstock		(¹)	(¹)	(¹)	(¹)	(²)	(²)	(²)	(³)	(³)	(⁴)
Method of feeding olefin	..	(²)									
Electrolyte, conc. moles H ₂ SO ₄ /liter	0.5	0	0	0	0	10	10	8	10	10	10
Amps, Avg.	0.048	0.0999	0.0831	0.078	0.046	0.061	0.061	0.061	0.061	0.061	0.0389
Temperaturo, °F.	180	180	150	185	180	180	180	180	180	180	180
Volts vs. std. H ₂ Ref., 4V.	-0.87	-0.74	-0.89	-0.88	-1.44	-1.44	-1.44	-1.44	-1.44	-1.44	-1.64
Load volts polarization vs. std. H ₂ ref.											
Ketone produced	..	0.93	0.69	0.79	0.78	1.38	0.98	1.54	1.54	1.54	1.54
Product selectivity to ketone	..	(¹⁰)									
Reaction time, hrs.	70	18.3	> 75	> 70	> 80	> 50	> 50	> 50	> 90	> 90	> 90
		70	90.8	42	24	24	24	24	21	21	72

(¹) Butene-2.(²) Butene-1.(³) Pentene-2.(⁴) Hexene-2.(¹⁰) C₄ Methyl ethyl ketone.(¹¹) C₅ Methyl propyl ketone.(¹²) C₆ Ketone.(¹⁰) Gas over surface of electrolyte.(²¹) Gas bubbled through electrolyte.(²²) PreadSORBED at 75° F.(²³) PreadSORBED at 120° F.

EXAMPLE 9.

Isobutylene was converted to acetone in accordance with the process of the preceding examples. The selectivity to ketone was 5 not as great as with *n*-butylenes.

EXAMPLE 10.

Employing a processing unit in accordance with the flowplan of Figure 3 methyl ethyl ketone is produced from *n*-butylenes from a mixed C₄ hydrocarbon stream utilizing 65 wt. % sulfuric acid to extract isobutylene from the stream at temperatures in the range of 70 to 100° F. in a three stage mixer-settler extraction unit. The unabsorbed portion of 10 the hydrocarbon stream comprising *n*-butane, isobutane, and *n*-butylenes in a volume per cent ratio of 10/40/35 is passed directly to 15 the electrochemical reactor to convert the *n*-butylenes to methyl ethyl ketone.

20 Separate runs are made employing acid concentrations in the electrolyte of the electrochemical reactor (fuel cells) of 25, 45 and 65 wt. % H₂SO₄, respectively. The temperature of the reactor is operated in 25 separate runs at 120°, 180° and 250° F.

In a run employing 5 wt. % H₂SO₄ electrolyte and an operating temperature of 30 120° F. methyl ethyl ketone is produced and removed continuously from the cells as a bottoms stream with electrolyte, secondary butanol, and butanes. This stream is passed to the product recovery unit and subjected to distillation to separate the butanes. A crude methyl ethyl ketone containing 35 secondary butanol is passed to a ketone purification unit from whence the secondary butanol is separated and recycled to the electrochemical reactor. The electrolyte recovered from the aforementioned distillation 40 is recycled from the aforementioned product recovery unit to the electrochemical reactor.

In another run the cell is operated at 45 180° F. with a 45 wt. % H₂SO₄ electrolyte. Methyl ethyl ketone and butanes are recovered overhead and separated.

The term "anodic oxidation" as employed herein shall be understood to include anodic dehydrogenation.

The terms "electrochemical cell" and 50 "electrochemical reactor" as employed herein shall be construed to include both power-generating fuel cells as hereinbefore defined and electrolytic cells which are driven by an external source of direct electrical current.

WHAT WE CLAIM IS:—

1. A process for producing a ketone which comprises introducing the corresponding olefin or the corresponding secondary alcohol to an electrochemical cell containing 60 an aqueous sulfuric acid electrolyte, subjecting said olefin or alcohol to anodic oxidation therein while in contact with said electrolyte and recovering said ketone from said electrolyte.

2. A process in accordance with Claim 1 wherein said electrochemical cell is a power producing fuel cell containing an anode and a cathode in contact with said electrolyte wherein oxygen is admitted into dual contact with said cathode and said electrolyte.

3. A process in accordance with Claim 1 wherein said electrochemical cell is an electrolytic cell containing an anode and a cathode in contact with said electrolyte and wherein a direct electrical current is admitted to said cathode from outside said cell.

4. A process in accordance with any of Claims 1—3 wherein the acid concentration of said electrolyte is in the range of 0.5 to 12 moles H₂SO₄/liter, preferably 6 to 11.5 moles/liter.

5. A process in accordance with Claim 4 wherein the acid concentration of said electrolyte is in the range of 9 to 10.5 moles/litre.

6. A process in accordance with any of Claims 1—5 wherein said electrolyte is maintained at a temperature in the range of 75° F. to 250° F., preferably 120° F. to 185° F.

7. A process in accordance with any of Claims 1—6 wherein said electrolyte is maintained at a pressure in the range of 1 to 50 atmospheres.

8. A process in accordance with any of Claims 1—7 wherein the feedstock is passed into dual contact with said electrolyte and an anode of an electrochemical cell wherein the oxidation potential at said anode is maintained in the range of 0.5 to 1.65 volts anodic to standard hydrogen reference, and said ketone is recovered from said electrolyte.

9. A process in accordance with any of Claims 1—8 wherein said ketone is separated from said electrolyte and said cell as a gas.

10. A process in accordance with any of Claims 1—8 wherein said cell is operated at 105 a temperature below the boiling point of said ketone and said ketone is removed from said cell as a liquid with said electrolyte.

11. A process in accordance with any of Claims 1—10 wherein said anode comprises 110 platinum.

12. A process according to any of Claims 1, 2, or 4 to 11, wherein said electrochemical cell is a fuel cell comprising an anode and a cathode for the adsorption and de-adsorption 115 as ions of a liquid fuel and oxygen respectively, said electrolyte providing ionic conductance between said anode and said cathode and conducting means external to said electrolyte adapted to admit of electron transfer from said anode and electron transfer to said cathode, and wherein said alcohol is passed into dual contact with said anode and said electrolyte, oxygen gas is passed into dual contact with said cathode and said electrolyte, said ketone is continuously recovered from said electrolyte, and electrical energy generated in said cell is recovered.

13. A process in accordance with any of

- Claims 1 to 12 wherein the alcohol is a C₃ to C₈ aliphatic alcohol.
14. A process in accordance with Claim 13 wherein said alcohol is isopropanol, said ketone is acetone, and an isopropanol to acetone ratio is maintained in said electrolyte of greater than 20/1 by separating said acetone, as it is formed, from said electrolyte.
15. A process in accordance with Claim 13 wherein said alcohol is butanol-2, said ketone is methyl ethyl ketone and the ratio of alcohol to ketone maintained in said electrolyte is at least 1/3.
16. A process in accordance with Claim 13 wherein said alcohol is pentanol-2, said ketone is methyl propyl ketone and the ratio of alcohol to ketone maintained in said electrolyte is at least 1/3.
17. A process in accordance with any of Claims 13 to 16 wherein the alcohol concentration is at least 0.5, preferably at least 5 moles/liter.
18. A process in accordance with any of Claims 1 to 11 where said olefin is a C₃ to C₁₂ normal olefin.
19. A process in accordance with any of Claims 1 to 11 for converting a normal olefin to the corresponding ketone which comprises contacting a hydrocarbon mixture containing an iso-olefin, a paraffin and said normal olefin with a first aqueous sulfuric acid solution, selectively absorbing said iso-olefin in said acid, separating the resulting iso-olefin-acid extract from said paraffin and said normal olefin, passing said paraffin and said olefin in gaseous form into a second aqueous sulfuric acid solution which comprises the electrolyte of an electrochemical cell containing a cathode and a platinum comprising anode (as hereinbefore defined), maintaining an oxidation potential at said anode in the range of 0.5 to 1.65 volts anodic to standard hydrogen reference and recovering said ketone and said paraffin from said electrolyte.
20. A process for producing a ketone substantially as hereinbefore described in any one of the Examples.
21. A ketone when produced by a process in accordance with any preceding claim.

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including ketone, which comprises a hydrocarbon mixture containing paraffin and said normal olefinic quinones, sulfuric acid solution, and asurbing said ion-selecting the resulting iso-olefin-olefin and paraffin and said normal said paraffin and said olefin distilling into a second aqueous sulfuric acid solution which comprises the electrolyte a technical cell containing a cathode comprising anode (as herein maintained an oxidation anode in the range of 0.3 anode to standard hydrogen recovering said ketone and said electrolyte. uses for producing a ketone 45 4 are hereinbefore described in Examples. which produced by a process with any preceding claim.

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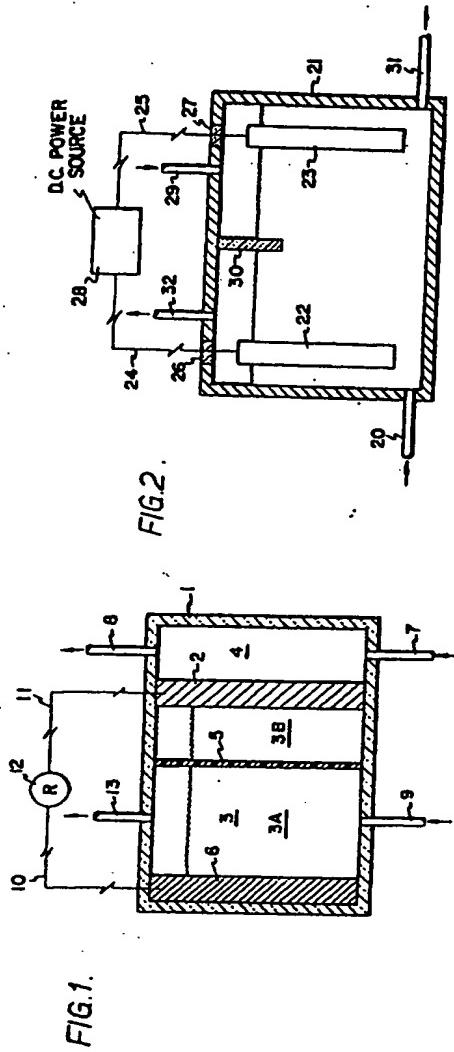


FIG. 1.

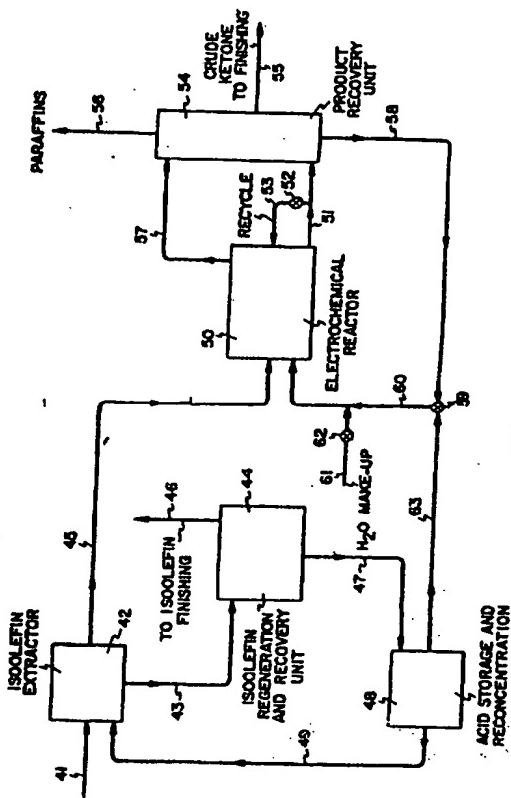


FIG. 3

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